National Defence
Research and Development Branch

Défense Nationale
Bureau de Recherche et Développment

TECHNICAL MEMORANDUM 85/203
February 1985

MULTITEMPERATURE PYROLYSIS GAS CHROMATOGRAPHY FOR THE IDENTIFICATION OF ELASTOMERIC MATERIALS

R.M. Morchat - P.M. Mahoney

Defence Research Establishment Atlantic

Centre de Recherches pour la Défense Atlantique

Canada

85-3264/

TERMS OF RELEASE

THIS DOCUMENT CONTAINS PROPRIETARY INFORMATION. IT IS FURNISHED IN CONFIDENCE AND WITH THE EXPRESS UNDERSTANDING THAT PROPRIETARY AND PATENT RIGHTS WILL BE RESPECTED.

PLEASE ADDRESS FURTHER ENQUIRIES TO:

THE CHIEF,
DEFENCE RESEARCH ESTABLISHMENT ATLANTIC,
P.O.BOX 1012, DARTMOUTH, N.S., B2Y 3Z7
CANADA.

DEFENCE RESEARCH ESTABLISHMENT ATLANTIC
9 GROVE STREET P.O. BOX 1012
DARTMOUTH, N.S.
B2Y 3Z7

TELEPHONE
(902) 426-3100

CENTRE DE RECHERCHES POUR LA DÉFENSE ATLANTIQUE
9 GROVE STREET C.P. 1012
DARTMOUTH, N.É.
B2Y 3Z7

National Defence
Research and Development Branch

Défense Nationale
Bureau de Recherche et Développement

MULTITEMPERATURE PYROLYSIS GAS CHROMATOGRAPHY FOR THE IDENTIFICATION OF ELASTOMERIC MATERIALS

R.M. Morchat - P.M.Mahoney

February 1985

Approved by B.F. Peters A/Director/Technology Division

DISTRIBUTION APPROVED BY

A/D/TD

TECHNICAL MEMORANDUM 85/203

Defence Research Establishment Atlantic

Centre de Recherches pour la Défense Atlantique

Canada

ABSTRACT

The feasibility of using a single column multitemperature pyrolysis gas chromatographic (GC) approach, to provide for an unambiguous identification of eight classes of frequently encountered elastomers, was investigated. Pyrograms of these eight classes of standard elastomers were obtained at three pyrolysis temperatures, 600°C, 800°C and 995°C, and constituted a reference file. The identification of an unknown elastomer was accomplished by comparison of the times and relative intensities of the major peaks in the pyrograms generated at the three pyrolysis temperatures.

RÉSUMÉ

On a étudié la faisabilité d'analyser par chromatographie en phase gazeuse (CG) sur colonne simple les produits de pyrolyse obtenus à plusieurs températures, pour identifier sans équivoque huit catégories d'élastomères fréquemment rencontrés. On a obtenu les pyrogrammes de ces huit catégories d'élastomères standard à trois températures, soit 600°C, 800°C et 995°C; ces pyrogrammes ont ensuite servi de pyrogrammes de référence. On a identifié un élastomère inconnu en comparant le temps et l'intensité des principaux pics sur les pyrogrammes obtenus aux trois températures de pyrolyse.

TABLE OF CONTENTS

	Page No.
ABSTRACT	ii
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	3
PYROLYSIS MECHANISMS	3
RESULTS AND DISCUSSION	4
CONCLUSION	7
TABLES	9
FIGURES	13
REFERENCES	21
DOCUMENT CONTROL DATA - R & D	23

INTRODUCTION

DREA Dockyard Laboratory is frequently asked to analyze and identify elastomeric materials. These identifications are required to ensure that correct materials are used for replacement parts. Also, in the area of elastomer selection based on the criterion of fire safety, analysis and identification is required to ensure that the best elastomers are identified and utilized.

The analysis and identification of elastomeric materials can be performed by the application of physical tests and chemical methods. However, due to a variety of short-comings with these techniques, which will be detailed in this paper, a simpler method which would be both time and cost effective and which would also provide for unambiguous identification of the elastomeric materials was required.

The classical chemical method[1,2] used to identify elastomeric materials involves the fusion of elemental sodium with the polymer followed by a series of chemical tests which provides an elemental analysis for nitrogen, sulfur and chlorine and allows for initial grouping as outlined in Table 1. Further grouping and identification of the elastomers is accomplished by following a systematic step-by-step wet chemical analysis approach as outlined in Table 2.

This classical approach, however, is inherently prone to error at both the elemental analysis step and during the step-by-step wet chemical procedure. If, for example, an incomplete fusion of the elastomer and elemental sodium takes place, then an incorrect appraisal of the elements present in the elastomer will be obtained. Further, the classical analytical method is also very time consuming and requires a large amount of sample such that non-destructive evaluations are not possible.

A method which would provide accurate identification of an elastomeric material with no ambiguities and require only a small quantity of sample would therefore be more useful to the materials scientist. One such technique which could be used is pyrolysis infrared spectroscopy[3,4]. However, this involves separate pyrolysis and analysis steps and requires a relatively large sample (2g) which could result in unacceptable damage to the elastomeric part being identified.

Another technique which can better satisfy the needs of the materials scientist is pyrolysis gas chromatography (GC)[5-11]. The basic concept of using thermal degradation of a non-volatile material to obtain fragmentation into volatile components followed by gas chromatographic analysis is a relatively recent analytical technique. The basic approach involves obtaining a characteristic pyrogram (pyrolysis-chromatogram) of a known material and then using this pyrogram as a standard in a reference file. Identification of an unknown material is then based on the visual comparison (best fit) of the pyrogram generated from the unknown with pyrograms compiled in the reference file.

When the pyrogram of the unknown is indistinguishable from more than one pyrogram in the reference file, the usual procedure is to reapply pyrolysis GC, using several different gas chromatographic column packing materials and procedures. It is then possible to establish a series of reference files for each standard material which contains a set of pyrograms that differ in overall appearance due to the altered retention times of the pyrolysis products. Using the set of reference pyrogram files thus generated for each standard material, accurate identification of the unknown material is then possible.

Although this pyrolysis GC approach is far superior to the classical wet-chemistry method in providing positive identification of elastomeric materials, it, however, also has some disadvantages. To obtain the required set of pyrograms, several GC columns must be interchanged and sufficient time must be allowed between these changes to provide for stabilization of the instrument's operating conditions. Further, the GC columns are glass and are prone to damage from constant handling.

An alternative pyrolysis GC approach, which overcomes these disadvantages, has been investigated and will be outlined below. The thermal fragmentation of organic molecules is known to be temperature dependent. Therefore, rather than switching to different GC column packing materials to generate visibly different pyrograms of a standard material, variation of the pyrolyzing temperature was used to generate visibly different pyrograms while still utilizing the same GC column packing material.

The aim of this study was therefore to address the feasibility of using a single GC column packing material and only changing the pyrolyzing temperature to obtain a series of pyrograms to identify elastomeric materials unambiguously.

EXPERIMENTAL PROCEDURE

A Pyroprobe Model 170 (Chemical Data Systems, Oxford, Pa) heated-filament pyrolysis unit equipped with a platinum coil probe and quartz tube (25 mm long, 2.5 mm OD, 2.0 mm ID), was used to pyrolyze small quantities (approximately 1 mg) of elastomeric samples for gas chromatographic analysis. A Varian 4600 GC and Vista 401 data system was used to analyze the pyrolysis products. Separation of the products was achieved using temperature programming and a glass column (1 m x 4 mm ID) packed with Chromosorb 102 (Supelco Inc.). Operating conditions for the pyrolyzer and GC are shown in Table 3. The Vista 401 stored the raw data on micro floppy disks and produced the pyrogram and results page.

Eight classes of frequently evaluated elastomers, listed in Table 4, were selected to be evaluated. Pyrograms were obtained at the three pyrolysis temperatures of 600°C, 800°C and 995°C.

PYROLYSIS MECHANISMS

During pyrolysis polymeric materials such as elastomers undergo thermal degradation which cleaves the material into lower molecular weight fragments. The location of the initial bond cleavage in a thermally excited polymer is characteristic of that polymer. In fact, once the critical pyrolysis temperature is exceeded, depolymerization which is essentially the reverse of addition polymerization, occurs. This results in the successive release of monomeric units from the end of the polymer chain.

In addition, random degradation where bonds between elements in the polymeric chain are cleaved at random, can occur. In fact, through various intermolecular events, products with an increased molecular weight can also be formed.

These processes of thermal degradation are based on three steps: initiation, propagation and termination[12,13]. In the initiation step, sufficient thermal energy must be supplied to the polymer to cleave a bond and form a polymeric radical (R·):

$$\text{Polymer} \longrightarrow R\cdot$$

In the propagation step the polymeric radical cleaves again to give a monomer unit and a different polymeric radical ($R_1\cdot$). This release of monomer units can continue until only monomer remains:

$$R\cdot \longrightarrow \text{Monomer} + R_1\cdot$$

$$R_1\cdot \longrightarrow \text{Monomer} + R_2\cdot$$

etc

$$R_i\cdot \longrightarrow \text{Monomer}$$

A competing step is the termination step whereby two polymeric radicals combine to form a polymeric fragment which differs in molecular weight from the original polymer:

$$R_x\cdot + R_y\cdot \longrightarrow \text{Polymeric Fragment}$$

This polymeric species may fragment in a manner similar to the original polymer.

The outcome of this fragmentation process is very dependent on the pyrolysis conditions. In general, the higher the pyrolysis temperature, the greater the fragmentation of the polymeric material[10]. Therefore, there should be an increase in the complexity of the generated pyrograms as the pyrolysis temperature is increased.

RESULTS AND DISCUSSION

The ASTM[14] designated practice for coding and classifying elastomers, according to the chemical composition of the polymer chain, results in 43 different rubbers being identified. However, a large majority of these 43 different types of rubbers are special application materials and are not found in common usage. As a result, only eight classes of frequently encountered elastomers, which are outlined in Table 4, were selected to be evaluated by application of multitemperature pyrolysis GC.

The pyrograms obtained for these eight different elastomers at the three pyrolysis temperatures of 600°C, 800°C and 995°C are found in Figures 1 to 8 and constitute the reference file on each type of elastomer. These

pyrograms showed good reproducibility of peak retention times: a maximum error of less than 2% was indicated. It might be added that the peak intensities of the pyrograms are related to the sample sizes and these were not kept constant in this work. The relative intensities of the peaks in each pyrogram are, however, significant.

No identification of the peaks in the pyrograms was attempted; however, this could be accomplished by manual collection of the GC effluent followed by spectroscopic analysis or, more effectively, by utilizing a mass spectrometer as the detector[15]. All of the peaks with retention times less than 1.5 minutes are similar and are due to smaller molecules such as carbon dioxide and methane which are formed when most elastomers are pyrolyzed. Likewise, peaks with retention times greater than 10 minutes are due to very high molecular weight species and are observed as broad peaks.

The differences in the multitemperature pyrograms, based on peak times and relative intensities are sufficient to provide for unambiguous identification of an elastomer. In fact, identification of an unknown elastomer is simply accomplished by use of visual comparison as the means of matching the pyrograms obtained from the unknown with those generated from the standard elastomeric materials.

Utilizing the criteria of peak time and relative intensity, an examination of the three pyrograms for Silicone rubber (Figure 1) indicates that they are quite distinctive from the pyrograms of the other elastomers in that they contain only two peaks: one at 7.5 minutes and the other at 9.3 minutes. Except for this material (silicone rubber), the pyrograms for the other elastomers contain a greater number of peaks which at first glance appear to make visual identification difficult. However, many salient differences in the pyrograms can be extracted when all three temperature pyrograms are used.

Figure 2 illustrates the effect of temperature on the complexity of the GC pyrograms of the earliest elastomer developed, natural rubber. At the pyrolysis temperature of 600°C only one major peak at 5.2 minutes, most likely due to the monomeric unit isoprene[8], was observed. Further, as the pyrolysis temperature was raised to 800°C and then to 995°C, the number of major peaks in the respective pyrograms increased as did the relative intensities of certain peaks. Examination of the pyrograms for Buna-N and Buna-S rubbers

(Figures 3 and 4 respectively) indicate that while their major peak at 10.0 minutes makes them distinct from the others, they are quite similar at 995°C. However, at the lower pyrolysis temperature of 600°C, Buna-N rubber retains its major peak at 8.5 minutes while Buna-S does not.

The other elastomers also have distinctive features: Neoprene rubber (Figure 5) displays a predominant peak at 6.5 minutes at the 600°C pyrolysis temperature. At this lower temperature, Urethane rubber (Figure 6) has its predominant peak at 8.5 minutes while Butyl rubber (Figure 7) has a major peak at 7.4 minutes. The pyrograms for Ethylene-Propylene rubber (Figure 8) remain multipeaked at all three pyrolysis temperatures.

In addition to the dominant features outlined above, there are a number of more subtle differences between pyrograms which would help to confirm analyses. For example, for Urethane rubber (Figure 6) a major peak at 4.0 minutes decreases in height relative to the others as the pyrolysis temperature is decreased. Such a peak decrease is also observed for the 5.8 minute peak of Butyl rubber (Figure 7). Additionally, the doublet of peaks at 3.5 and 3.7 minutes in the pyrogram for Ethylene-Propylene rubber (Figure 8) at 995°C is not noted at the lower pyrolysis temperature of 600°C.

It can be seen that the 995°C pyrograms from some of the eight elastomers evaluated in this report are sufficiently different to be specific for the given material (Silicone rubber for example). However, no one pyrolysis temperature is adequate to allow for identification of all eight classes of elastomers and multitemperature analysis is required.

This multitemperature pyrolysis GC approach to elastomer identification has some disadvantages. It cannot be used to identify elastomers with complicated compositions of polymers since the sum of the peaks from the contributing polymers can result in an indistinguishable pyrogram. Also, the pyrolysis temperatures and GC column packing material chosen in this study were adequate to identify the eight classes selected, but they may not be optimum for other classes of elastomers. It should also be added that inter-laboratory reproducability is difficult to achieve since different operator techniques and different instruments may be used.

This multitemperature pyrolysis GC procedure could be improved by incorporating an identification step whereby the individual pyrolysis products were subjected to analysis by a mass spectrometer. This would allow for the range of elastomers and plastics to be enlarged and it would also allow for the detection and identification of blended products.

CONCLUSION

It has been shown in this study that a single column multitemperature pyrolysis GC approach provides for the unambiguous identification of eight classes of frequently encountered elastomers. . Identification of an unknown elastomer is accomplished by comparing the peak times and relative peak intensities of pyrograms produced at 995°C, 800°C and 600°C with pyrograms produced at the same temperatures from elastomer standards.

TABLE 1

SYSTEMATIC APPROACH TO ELASTOMER IDENTIFICATION

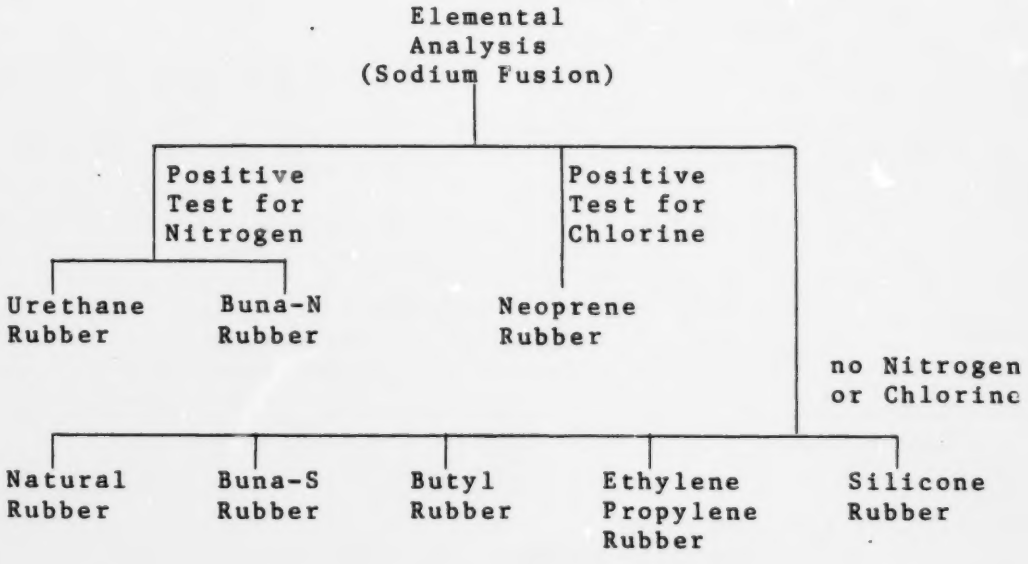

TABLE 2

CLASSIC CHEMICAL METHOD TO ELASTOMER IDENTIFICATION

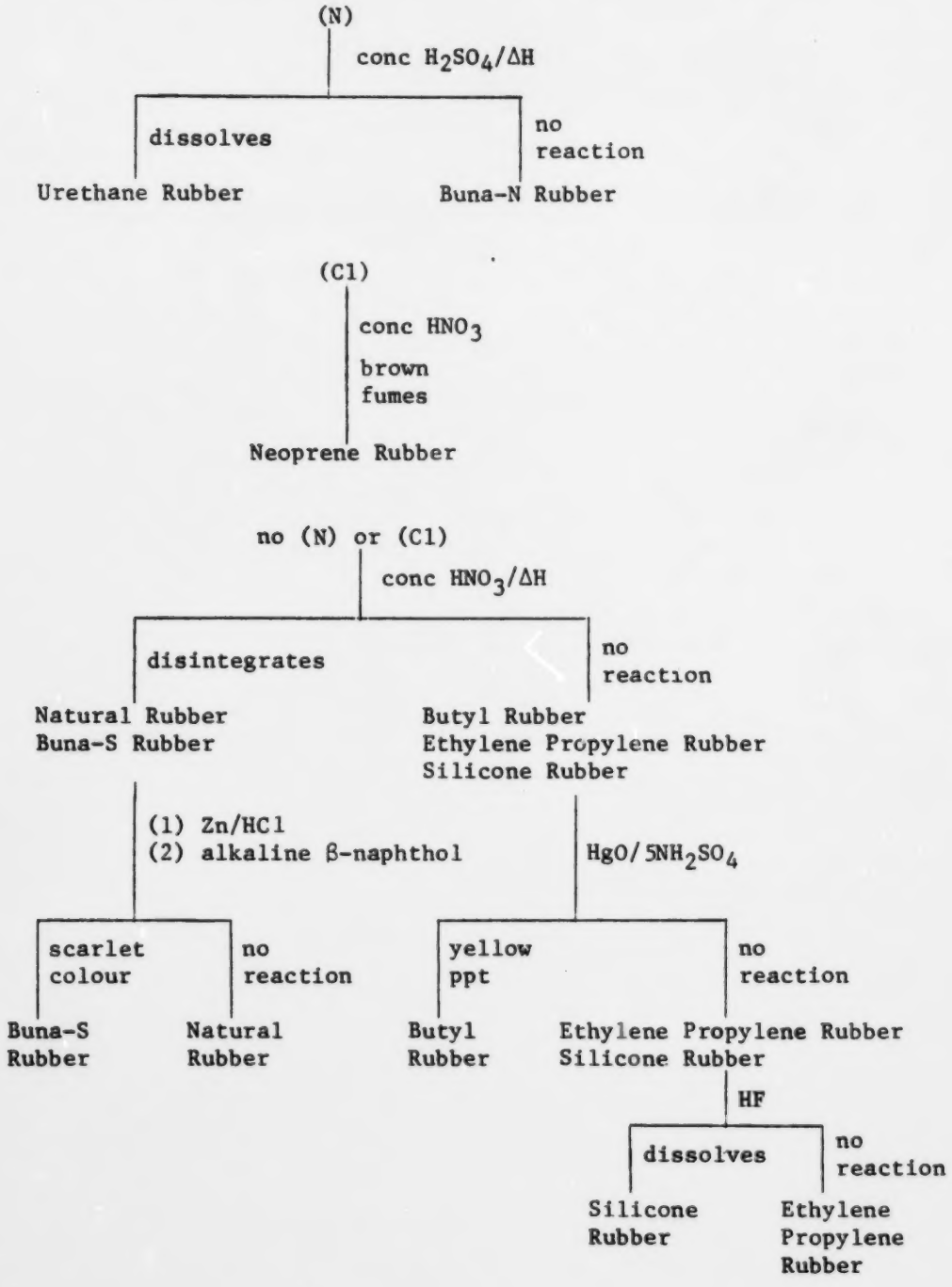

TABLE 3

PYROLYZER - GAS CHROMATOGRAPH OPERATING CONDITIONS

Pyroprobe Model 170	
Pyrolysis temperature	600°C, 800°C or 995°C
Pyrolysis chamber temperature	100°C
Ramp (temperature rise)	20°C/msec
Interval (pyrolysis time)	10 sec
Varian 4600 GC	
Injector temperature	100°C
FID cell temperature	300°C
Column oven	
initial temperature	50°C
post injection interval	1 min
temperature program	20°C/min linear
upper temperature	200°C
upper temperature interval	15 min
Flow rate ultra-pure nitrogen	30 mL/min

TABLE 4

CLASSES OF ELASTOMERS (ASTM DESIGNATIONS)

CR	-	polychloroprene (Neoprene)
EDPM	-	terpolymer of ethylene, propylene and a non-conjugated diene (Ethylene Propylene)
EU	-	polyester based polyurethanes (Urethane)
IIR	-	copolymer of isobutene and isoprene (Butyl)
MQ	-	polydimethylsiloxane (Silicone)
NBR	-	nitrile rubber, copolymer of acrylonitrile and butadiene (Buna-N)
NR	-	poly-*cis*-isoprene (Natural)
SBR	-	copolymer of styrene and butadiene (Buna-S)

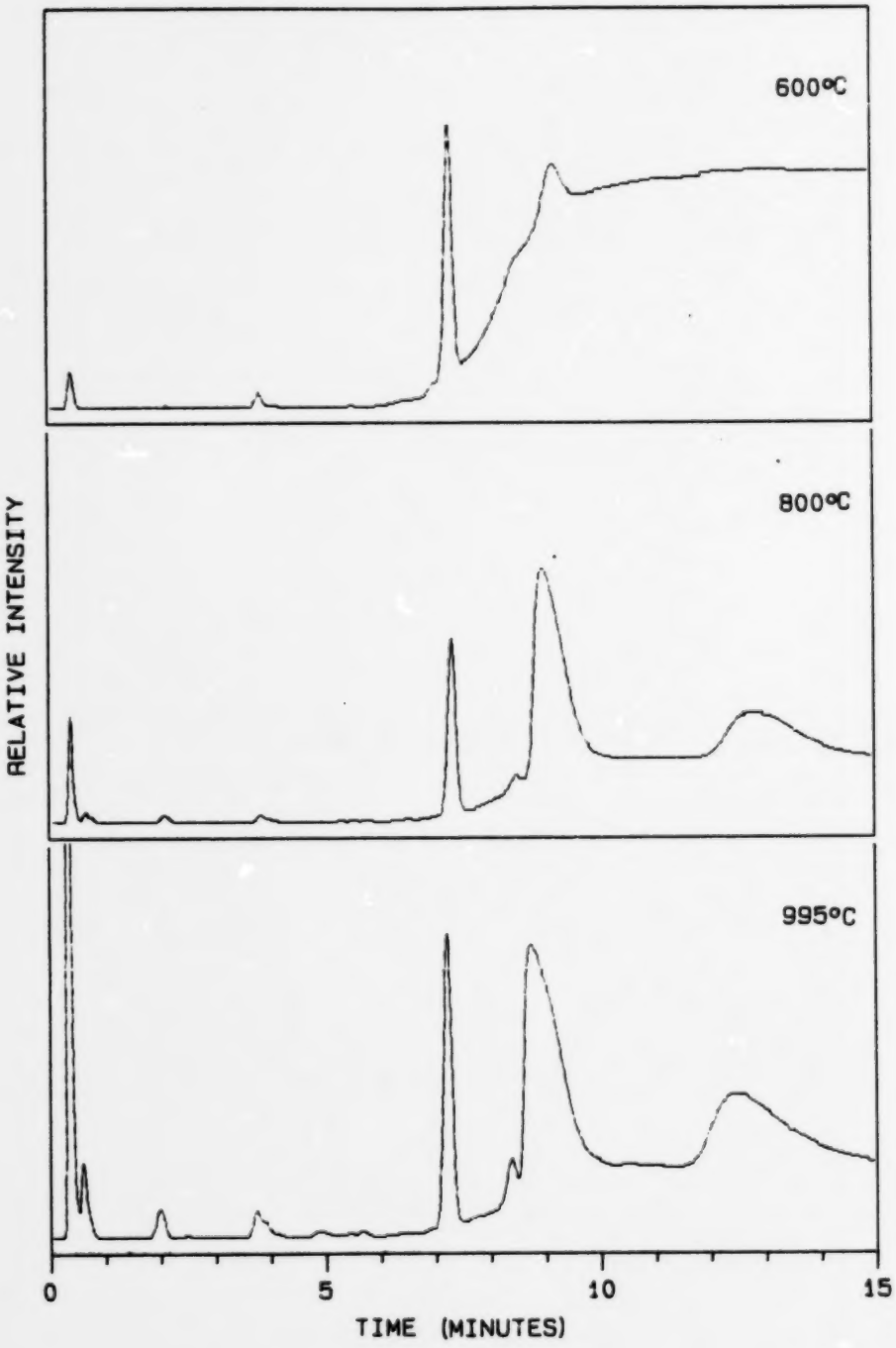

Figure 1: Pyrograms of Silicone Rubber (MQ) pyrolyzed at 600°C, 800°C and 995°C.

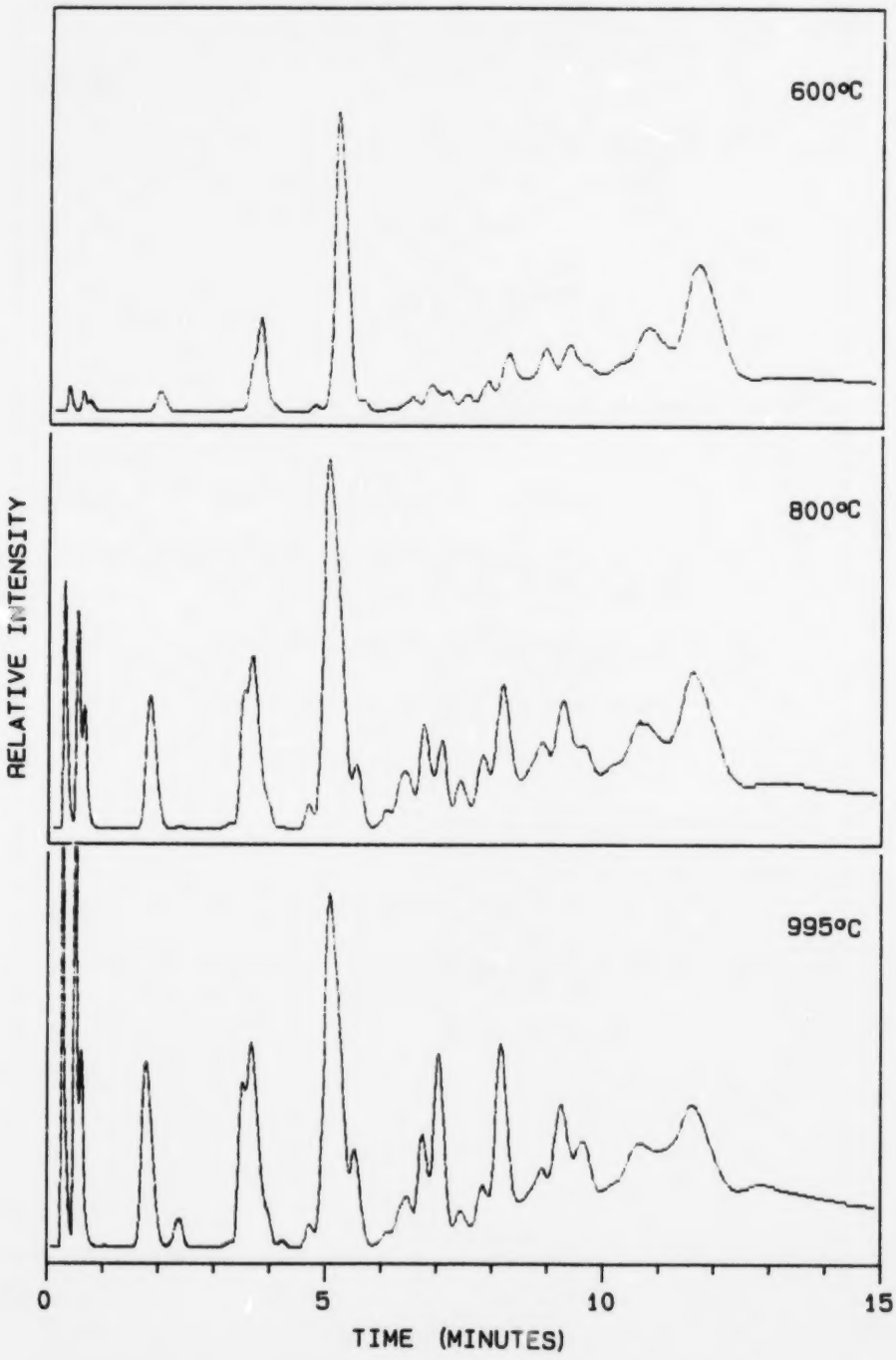

Figure 2: Pyrograms of Natural Rubber (NR) pyrolyzed at 600°C, 800°C and 995°C.

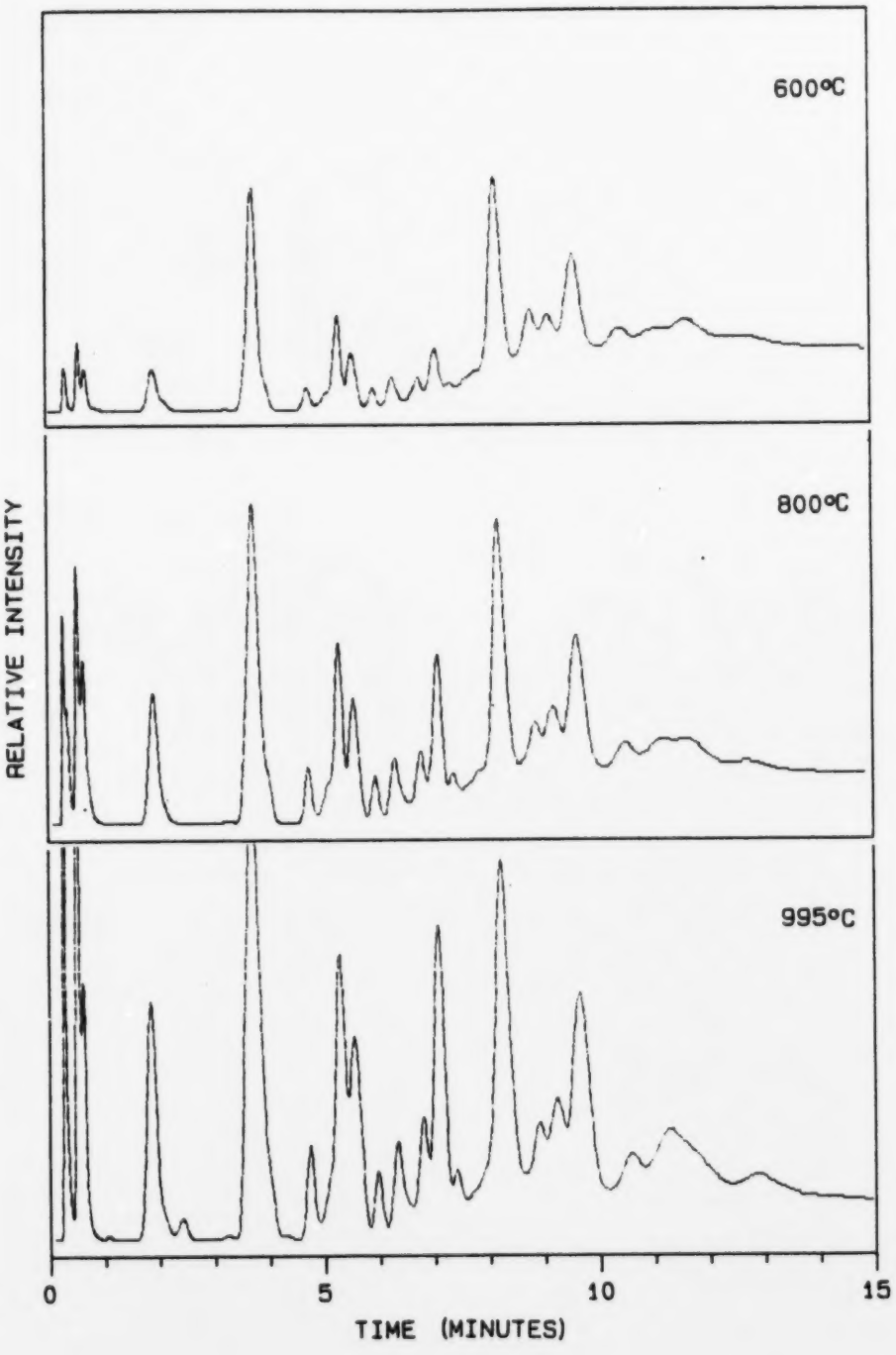

Figure 3: Pyrograms of Buna-N Rubber (NBR) pyrolyzed at 600°C, 800°C and 995°C.

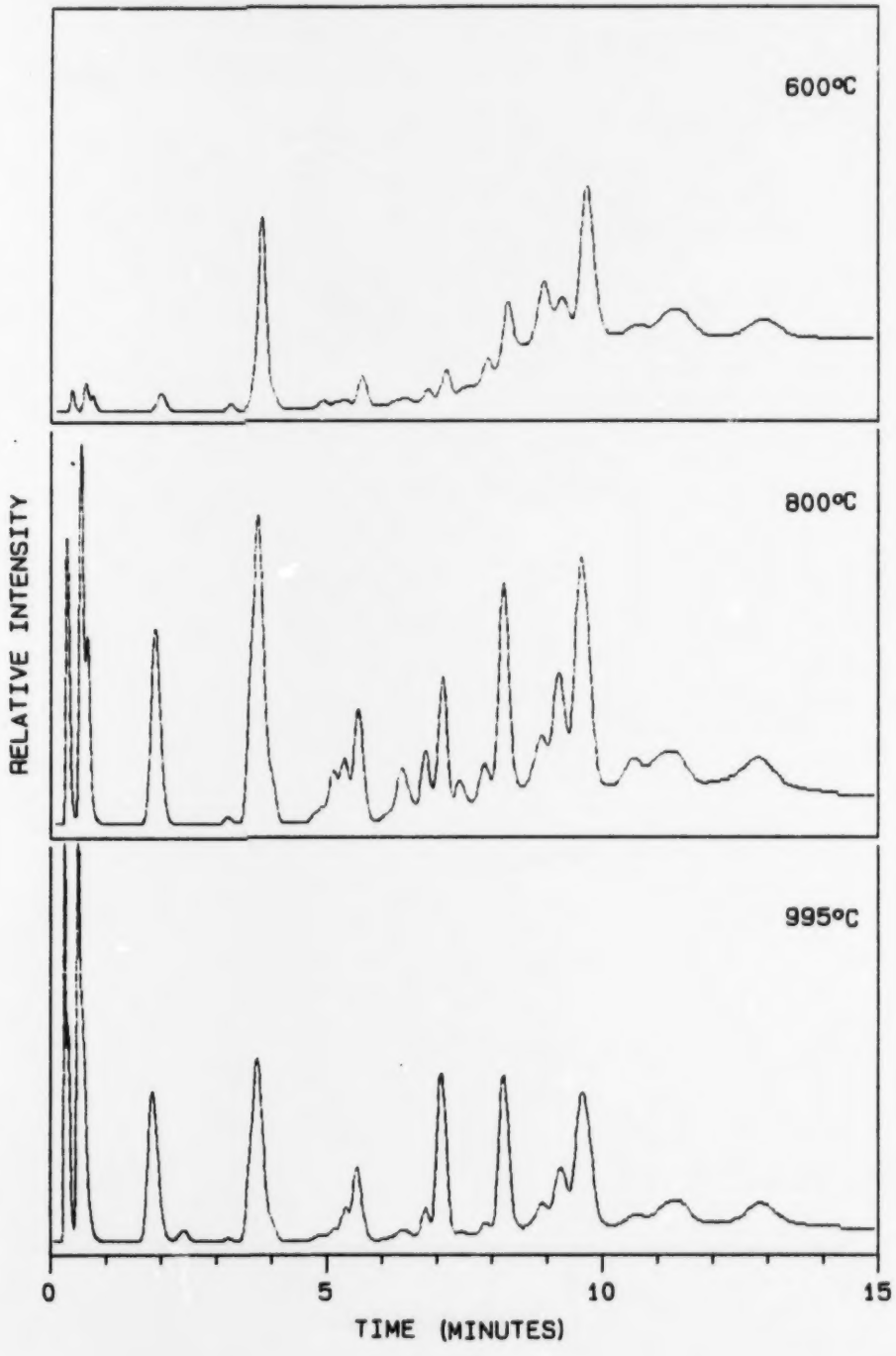

Figure 4: Pyrograms of Buna-S Rubber (SBR) pyrolyzed at 600°C, 800°C and 995°C.

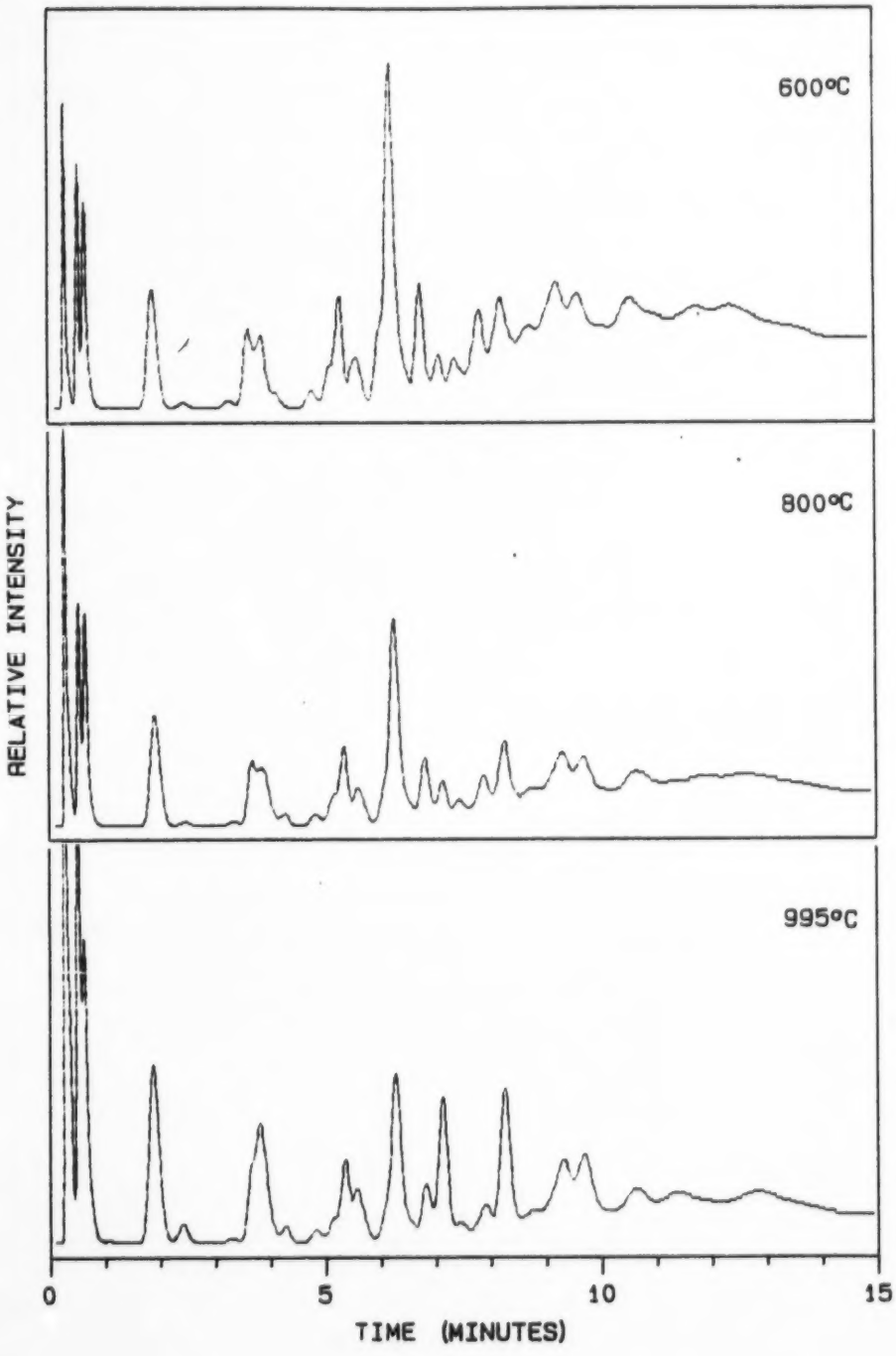

Figure 5: Pyrograms of Neoprene Rubber (CR) pyrolyzed at 600°C, 800°C and 995°C.

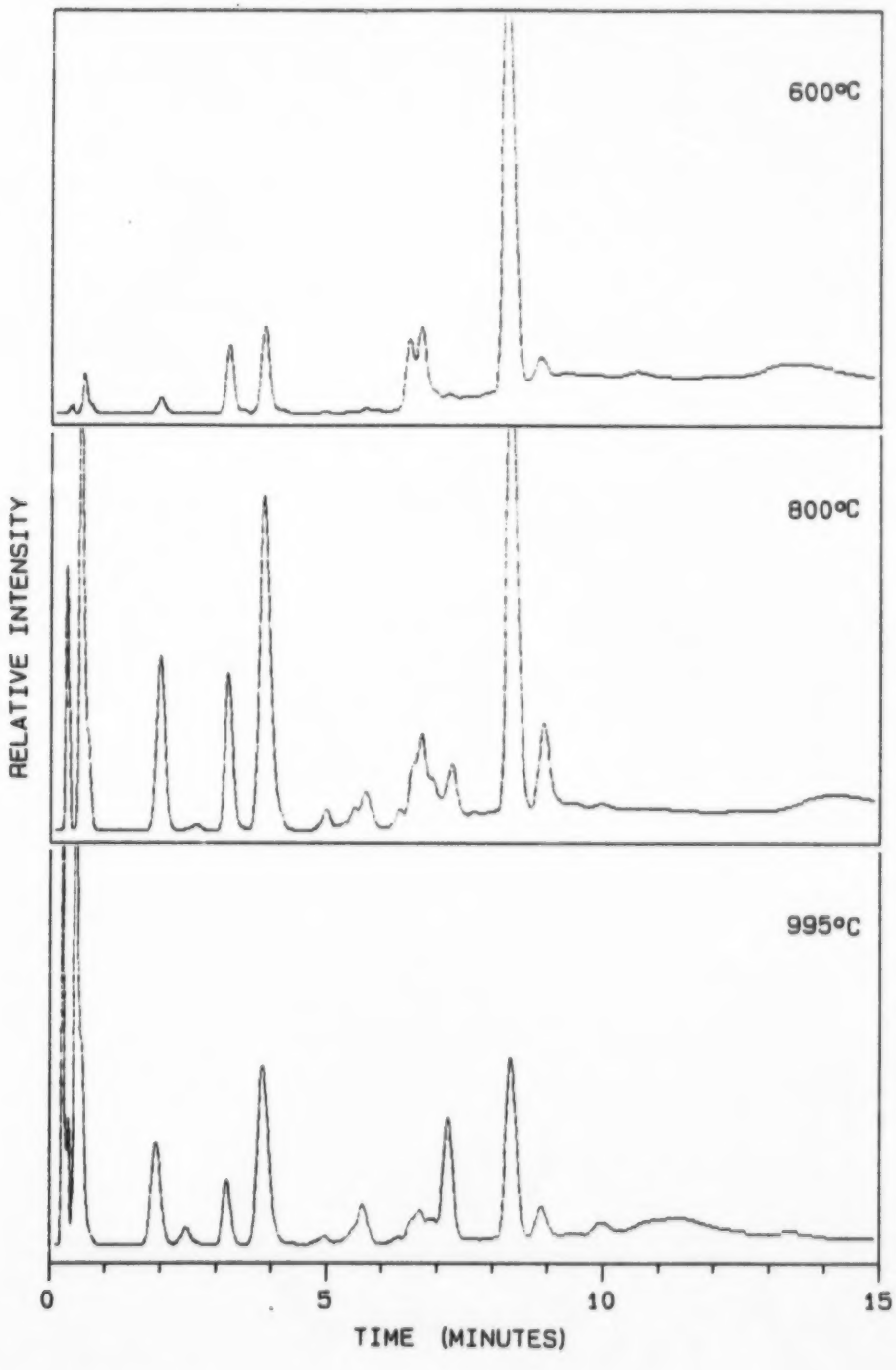

Figure 6: Pyrograms of Urethane Rubber (EU) pyrolyzed at 600°C, 800°C and 995°C.

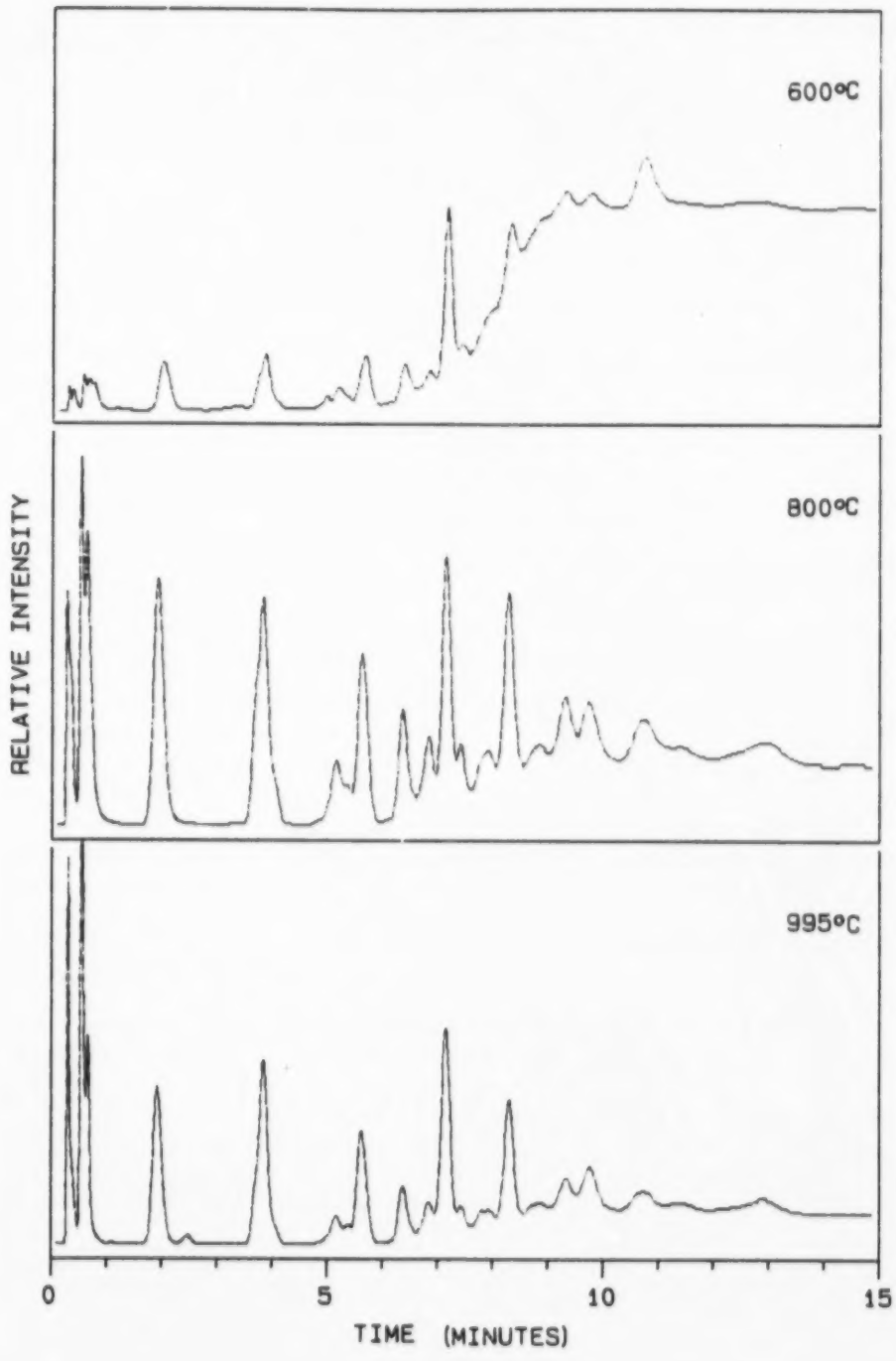

Figure 7: Pyrograms of Butyl Rubber (IIR) pyrolyzed at 600°C, 800°C and 995°C.

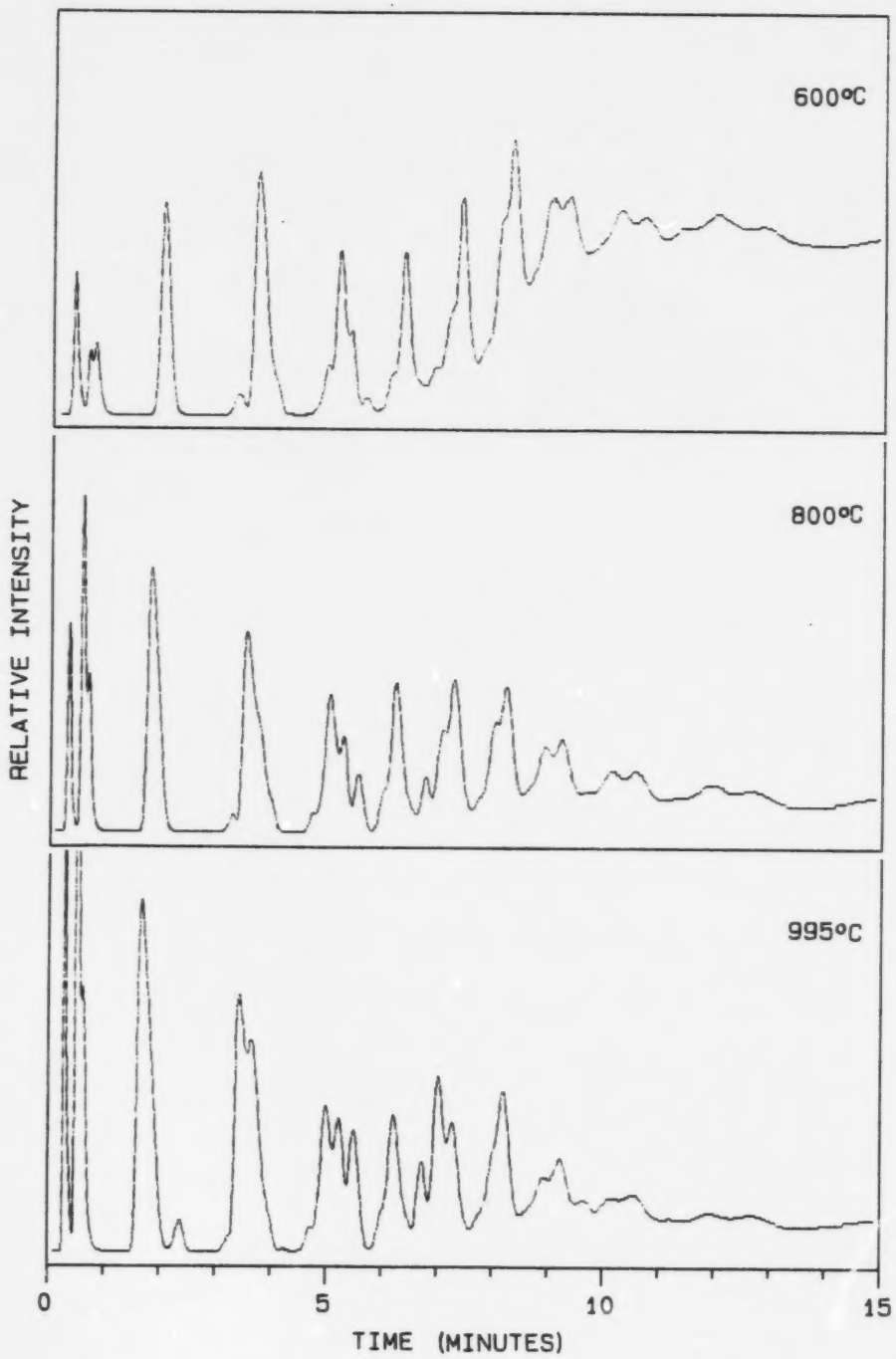

Figure 8: Pyrograms for Ethylene-Propylene Rubber (EPDM) pyrolyzed at 600°C, 800°C and 995°C.

REFERENCES

1. K.J. Saunders, "The Identification of Plastics and Rubbers", Chapman and Hall, Ltd., London, England, 1967.

2. C.A. Harper, "Handbook of Plastics and Elastomers", McGraw-Hill, 1975.

3. D.L. Harms, Anal. Chem., 25, 1140-55 (1953).

4. R.B.H. Sewell, G. Dodds and L.K. Yee, DREP Materials Report 76B, DREP, 1976.

5. R.W. May, E.F. Pearson and D. Scothern, "Pyrolysis Gas Chromatography", Heffers Printers Ltd., Cambridge, England, 1977.

6. R.B.H. Sewell and R.D. Rowland, DREP Materials Report 75-A, DREP, 1975.

7. B. Groten, Anal. Chem., 36, 1206-1212 (1969).

8. A. Krishen and R.G. Tucker, Anal. Chem., 46, 29-33 (1974).

9. J. Chih-AnHu, Anal. Chem., 49, 537-540 (1977).

10. E.M. Andersson and I. Ericsson, J. Anal. Appl. Pyrol., 2, 97-107 (1980).

11. W.H.T. Davison, S. Slaney and A.L. Wragg, Chem and Ind., 1356 (1954).

12. H. Sawada, "Thermodynamics of Polymerization", Cp 11, Marcel Dekker Inc., New York, NY, 1976.

13. C.J. Wolf, M.A. Grayson and D.L. Fanter, Anal. Chem., 52, 348A-358A (1980).

14. Standard Practice for Rubber and Rubber Latices - Nomenclature, Designation D1418, 1981.

15. J.L. Wuepper, Anal. Chem., 51, 997-1000 (1979).

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)

1. ORIGINATING ACTIVITY	2a. DOCUMENT SECURITY CLASSIFICATION
Defence Research Establishment Atlantic	Unclassified
	2b. GROUP

3. DOCUMENT TITLE

Multitemperature Pyrolysis Gas Chromatography for the Identification of Elastomeric Materials

4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Memorandum

5. AUTHOR(S) (Last name, first name, middle initial)

Morchat, Richard M. and Mahoney, Peter M.

6. DOCUMENT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
FEBRUARY 1985	26	15

8a. PROJECT OR GRANT NO.	9a. ORIGINATOR'S DOCUMENT NUMBER(S)
	DREA Technical Memorandum 85/203
8b. CONTRACT NO.	9b. OTHER DOCUMENT NO.(S) (Any other numbers that may be assigned this document)

10. DISTRIBUTION STATEMENT

11. SUPPLEMENTARY NOTES	12. SPONSORING ACTIVITY
	Defence Research Establishment (A)

13. ABSTRACT

The feasibility of using a single column multitemperature pyrolysis gas chromatographic (GC) approach, to provide for an unambiguous identification of eight classes of frequently encountered elastomers, was investigated. Pyrograms of these eight classes of standard elastomers were obtained at three pyrolysis temperatures, 600°C, 800°C and 995°C, and constituted a reference file. The identification of an unknown elastomer was accomplished by comparison of the times and relative intensities of the major peaks in the pyrograms generated at the three pyrolysis temperatures.

DSIS
78-078

Unclassified

Security Classification

KEY WORDS

gas chromatography

pyrolysis

elastomer identification

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the organization issuing the document.

2a. DOCUMENT SECURITY CLASSIFICATION: Enter the overall security classification of the document including special warning terms whenever applicable.

2b. GROUP: Enter security reclassification group number. The three groups are defined in Appendix 'M' of the DRB Security Regulations.

3. DOCUMENT TITLE: Enter the complete document title in all capital letters. Titles in all cases should be unclassified. If a sufficiently descriptive title cannot be selected without classification, show title classification with the usual one-capital-letter abbreviation in parentheses immediately following the title.

4. DESCRIPTIVE NOTES: Enter the category of document, e.g. technical report, technical note or technical letter. If appropriate, enter the type of document, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the document. Enter last name, first name, middle initial. If military, show rank. The name of the principal author is an absolute minimum requirement.

6. DOCUMENT DATE: Enter the date (month, year) of Establishment approval for publication of the document.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the document.

8a. PROJECT OR GRANT NUMBER: If appropriate, enter the applicable research and development project or grant number under which the document was written.

8b. CONTRACT NUMBER: If appropriate, enter the applicable number under which the document was written.

9a. ORIGINATOR'S DOCUMENT NUMBER(S): Enter the official document number by which the document will be identified and controlled by the originating activity. This number must be unique to this document.

9b. OTHER DOCUMENT NUMBER(S): If the document has been assigned any other document numbers (either by the originator or by the sponsor), also enter this number(s).

10. DISTRIBUTION STATEMENT: Enter any limitations on further dissemination of the document, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this document from their defence documentation center."

(2) "Announcement and dissemination of this document is not authorized without prior approval from originating activity."

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document, even though it may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall end with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (TS), (S), (C), (R), or (U).

The length of the abstract should be limited to 20 single-spaced standard typewritten lines; 7½ inches long.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a document and could be helpful in cataloging the document. Key words should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context.